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The Crystal and Molecular Structure of 3-Acetoxy-9-hydroxy-17-norkauran-16-one

By George Ferguson and Wayne C. Marsh

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

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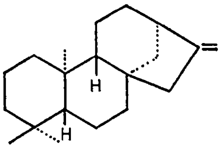
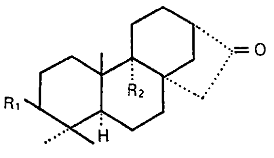
Crystals of the title compound are monoclinic, $a=11{\cdot}727$ (2), $b=7{\cdot}511$ (2), $c=21{\cdot}386$ (4) Å, $\beta=93{\cdot}90$ (1)°, $Z=4$, space group $C2$. The structure was solved by direct methods, and refined by least-squares procedures to $R=0{\cdot}054$ for 1015 reflexions. The molecule is characterized by a large amount of intramolecular steric crowding which largely determines the observed geometry. Rings *A*, *B*, *C*, and *D* have respectively chair, chair, distorted chair, and half-chair conformations. The molecules are linked in pairs about twofold axes by an O–H···O hydrogen bond [O···O 2·975 (7) Å].

Introduction

The kaurane family of diterpenes is of interest because of their wide occurrence in nature. The absolute configuration of *ent*-kaurene (I) has been established (Djerassi, Quitt, Mosettig, Cambie, Rutledge & Briggs, 1961) but little X-ray structural work has been reported for members of this diterpenoid series.



(I)



(II)

Microbial oxidation of 17-norkauran-16-one (II, $R_1=R_2=H$) by the fungus *Rhizopus nigricans* (McCrindle & Turnbull, 1975) produced a compound with secondary and tertiary hydroxyl groups. Chemical evidence strongly suggested C(3) as the site of the secondary hydroxyl and, somewhat less conclusively, C(9) as the site of the tertiary hydroxyl (II, $R_1=R_2=OH$).

The structure determination of the acetate derivative (II: $R_1=OCOCH_3$, $R_2=OH$) was undertaken to establish conclusively the sites of the microbial oxidation and to provide X-ray structural data, especially with respect to the bicyclic system, for this interesting diterpenoid series.

Experimental

The compound crystallized as irregularly shaped colourless prisms. Preliminary unit-cell parameters and space-group data were determined from various rotation, Weissenberg, and precession photographs; accurate cell parameters and orientation matrix were obtained by a least-squares procedure applied to 12 general reflexions measured on a Hilger and Watts diffractometer.

Crystal data

$C_{21}H_{32}O_4$, $M=348{\cdot}5$. Monoclinic, $a=11{\cdot}727$ (2), $b=7{\cdot}511$ (2), $c=21{\cdot}386$ (4) Å, $\beta=93{\cdot}90$ (1)°, $U=1879{\cdot}3$ Å^3, $D_c=1{\cdot}23$ g cm^{-3}, $Z=4$, $F(000)=760$. λ(Mo $K\alpha$) $=0{\cdot}71069$ Å, μ(Mo $K\alpha$) $=0{\cdot}90$ cm^{-1}. Systematic absences: hkl when $h+k$ is odd. Space group $C2(C_2^3)$, $Cm(C_s^3)$, or $C2/m(C_{2h}^3)$; $C2$ from the structure analysis.

The intensities of all reflexions with 2θ(Mo $K\alpha$) $<46°$ were measured on a PDP8-I controlled Hilger and Watts four-circle diffractometer with a scintillation counter and graphite monochromator. A θ/ω step scan was employed with 0·01° steps, a counting time of 1 s per step, and a scan width of 0·7° in θ. Background counts of 17·5 s were made at the beginning and end of each scan. The intensities of two standard reflexions, measured after every 100 reflexions, decreased very slowly over the period of data collection. Their final intensities were 98·5% of the original values. The data were corrected for the (slight) decomposition (assumed linear between standards); Lorentz and polarization factors were applied and the structure amplitudes derived. Of the 1429 unique data, 414 reflexions had a net count of less than 3σ above background and were excluded from the refinement, where $\sigma(I)$ is defined by $\sigma^2(I)=S+4(B_1+B_2)+(0{\cdot}01S)^2$ where S is the scan count and B_1 and B_2 are the background counts.

Structure analysis

The data were placed on an absolute scale (Wilson, 1942) and normalized structure amplitudes, E, were derived. The 225 largest E's were subsequently used as input into the multiple-solution program *MULTAN* (Germain, Main & Woolfson, 1971). The 3,3,13 and 1,1,10 reflexions were assigned starting phases of 0 and 45° respectively to fix the origin in space group $C2$ ($C2$ was chosen over the other possible space groups on the basis of the known optical activity of the compound). The assignment of 45° as the starting phase of the 1,1,10 reflexion additionally specified the enantiomorph. Additional symbolic phase selection by the program was unsatisfactory, yielding uninterpretable E maps. Because of this a manual expansion was carried out and the $20\overline{2}$ and $46\overline{2}$ reflexions were assigned symbolic phases; the starting values input into the tangent refinement procedure (Karle & Hauptman, 1956; Germain, Main & Woolfson, 1971) were $(0,\pi)$ and $(\pm\pi/4, \pm3\pi/4)$ respectively.

Owing to the absence of translational symmetry (lattice centring does not count as translational symmetry in this context) the conventional 'figure of merit' (Germain, Main & Woolfson, 1971) is unreliable as an indicator of the 'correctness' of a solution and the ψ_0 test of Cochran & Douglas (1955) is preferable. Of the resulting eight solutions only the two solutions with the lowest values of ψ_0 gave reasonable molecular fragments located in sensible positions in the unit cell. These two solutions were virtually identical.

A chemically reasonable fragment of eight atoms was used as input into the recycling procedure of Karle (1968). After two additional iterations some 18 atoms linked together in a chemically reasonable fashion had been located but the remainder of the molecule could not be found. Several attempts using different starting fragments were also unsuccessful. At this stage it was decided to try a step refinement program to see if some clue to the identity of any misplaced atoms could be discovered. Two cycles of refinement employing steps of 0·1 Å in the x, y, and z coordinates and 0·0063 Å^2 in U_{iso} substantially reduced the R value for the 18-atom fragment and indicated that two of the largest peaks in the original E map, common to all the trial structures, did not represent real atoms. These two atoms were omitted and the refined coordinates for the remaining 16 atoms were used as input into the recycling procedure. The subsequent E map revealed the entire molecule, the 25 atoms being amongst the 27 highest peaks in the map.

The refinement proceeded smoothly. Isotropic followed by anisotropic full-matrix least-squares refinement gave $R=\sum||F_o|-|F_c|/\sum||F_o|=0{\cdot}123$. The y coordinate of C(10) (Fig. 1) was held invariant to fix the origin in space group $C2$. A difference map at this point revealed unambiguously the positions of 28 of the 32 hydrogen atoms in the molecule. There was evidence that the C(21) methyl group was rotationally disordered and, while regions of electron density were present near the oxygen of the hydroxyl group, there was no obvious choice for the location of the hydroxyl hydrogen atom. Inclusion of the 28 unambiguously located hydrogen atoms in a structure-factor calculation gave an R of 0·074. The hydrogens were then included in the refinement with isotropic thermal parameters. During each cycle of the final refinement the scale and overall temperature factor were included in a 2 × 2 block while the molecule itself was divided into four approximately equal parts with the parameters of the atoms in each section included together in a separate block. This type of blocking resulted in more rapid convergence and more reasonable shifts for the hydrogen atom parameters than the conventional block-diagonal method.

The scattering factors for the C and O atoms were taken from *International Tables for X-ray Crystallography* (1962), and those for hydrogen from Stewart, Davidson & Simpson (1965). The weighting scheme employed in the final stages of refinement was $\omega=0$ for the unobserved reflexions and $\omega=1/[\sigma^2(F)+0{\cdot}001F^2]$ for the observed reflexions. The relative validity of the weighting scheme, as judged by the variation of $\omega\Delta^2$ over ranges of $\sin\theta/\lambda$ and $|F_o|$, was satisfactory. The final value of R was 0·054 for the 1015 observed reflexions and 0·087 for all 1429 reflexions. The final

Table 1. *Final fractional coordinates* ($\times 10^4$) *and anisotropic thermal parameters* (Å$^2 \times 10^2$) *for the carbon and oxygen atoms*

	x	y	z
O(1)	−1697 (4)	4456 (9)	4799 (2
O(2)	958 (4)	5340 (8)	6467 (2)
O(3)	1960 (4)	5344 (10)	9134 (2)
O(4)	3723 (5)	6189 (12)	8976 (3)
C(1)	1023 (7)	3378 (13)	7565 (3)
C(2)	1346 (8)	3428 (13)	8265 (4)
C(3)	1599 (6)	5297 (16)	8462 (3)
C(4)	594 (7)	6592 (13)	8347 (4)
C(5)	195 (6)	6460 (12)	7628 (3)
C(6)	−788 (8)	7663 (12)	7422 (3)
C(7)	−867 (9)	7911 (13)	6711 (4)
C(8)	−1036 (6)	6088 (11)	6373 (3)
C(9)	−146 (5)	4705 (10)	6619 (3)
C(10)	−28 (6)	4506†	7360 (3)
C(11)	−364 (6)	2919 (12)	6280 (4)
C(12)	−1617 (7)	2380 (13)	6091 (4)
C(13)	−2321 (6)	3987 (13)	5850 (3)
C(14)	−2292 (6)	5422 (14)	6362 (4)
C(15)	−982 (7)	6398 (12)	5646 (3)
C(16)	−1669 (6)	4885 (12)	5342 (3)
C(17)	−1087 (8)	3600 (14)	7619 (4)
C(18)	1009 (10)	8499 (16)	8467 (5)
C(19)	−375 (9)	6196 (22)	8790 (5)
C(20)	3014 (8)	5811 (14)	9317 (4)
C(21)	3202 (8)	5808 (18)	10029 (4)

† Held invariant to fix the origin in space group $C2$.

The anisotropic thermal parameters U_{ij} are terms in the expression $\exp\left[-2\pi^2(h^2a^*U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	5·9 (3)	6·6 (4)	3·5 (3)	−0·1 (3)	−0·1 (2)	−0·1 (3)
O(2)	3·0 (2)	6·0 (4)	4·2 (2)	−1·1 (3)	0·5 (2)	−0·4 (3)
O(3)	5·3 (3)	10·1 (5)	3·1 (3)	−0·6 (4)	0·1 (2)	1·4 (3)
O(4)	6·0 (4)	12·4 (7)	6·1 (4)	−2·2 (4)	−1·2 (3)	2·1 (4)
C(1)	4·8 (5)	5·3 (6)	3·8 (4)	1·3 (4)	−0·3 (4)	−0·1 (4)
C(2)	4·8 (5)	5·3 (7)	4·9 (5)	1·9 (5)	−0·3 (4)	0·4 (5)
C(3)	4·1 (4)	10·0 (8)	2·6 (4)	−0·3 (6)	−0·5 (3)	0·7 (5)
C(4)	5·0 (5)	6·3 (6)	3·8 (4)	0·3 (5)	0·7 (4)	0·3 (5)
C(5)	4·1 (4)	4·8 (5)	3·1 (4)	0·2 (4)	0·6 (3)	−0·2 (4)
C(6)	6·0 (5)	4·6 (5)	3·6 (4)	1·1 (5)	−0·4 (4)	−0·8 (4)
C(7)	6·8 (6)	4·4 (6)	5·0 (5)	1·1 (6)	−0·9 (4)	0·2 (5)
C(8)	4·1 (4)	3·8 (5)	3·7 (4)	0·3 (4)	−0·1 (3)	0·8 (4)
C(9)	2·3 (3)	3·9 (5)	3·0 (3)	−0·7 (4)	0·1 (3)	−0·4 (3)
C(10)	2·9 (4)	3·8 (5)	2·9 (3)	0·5 (4)	0·3 (3)	0·1 (4)
C(11)	4·5 (4)	3·8 (5)	3·8 (4)	0·1 (4)	−0·3 (4)	0·3 (4)
C(12)	4·9 (5)	5·4 (6)	6·0 (5)	−1·4 (5)	−0·3 (4)	2·1 (5)
C(13)	3·5 (5)	6·7 (7)	4·3 (4)	−1·8 (5)	−0·7 (3)	0·6 (4)
C(14)	3·9 (4)	5·8 (6)	4·2 (4)	1·8 (5)	0·3 (3)	1·0 (5)
C(15)	4·9 (5)	4·7 (5)	3·4 (4)	−0·5 (5)	0·4 (3)	0·9 (4)
C(16)	4·4 (4)	4·6 (6)	3·8 (5)	0·2 (4)	−0·6 (3)	1·1 (4)
C(17)	5·7 (5)	6·1 (6)	2·7 (4)	0·1 (5)	0·3 (3)	1·1 (4)
C(18)	7·9 (7)	7·0 (8)	5·3 (6)	−1·3 (7)	0·6 (6)	−0·8 (6)
C(19)	5·2 (5)	10·7 (9)	3·7 (5)	0·6 (7)	1·2 (4)	−0·6 (6)
C(20)	5·3 (5)	6·8 (7)	5·3 (5)	−0·6 (5)	−1·1 (4)	−0·2 (5)
C(21)	10·1 (7)	11·9 (9)	4·2 (4)	−0·7 (8)	−1·8 (5)	1·6 (6)

weighted $R\{[\sum\omega(F_o-F_c)^2/\sum\omega F_o^2]^{1/2}\}$ was 0·060 while the error in an observation of unit weight was 1·290. Final positional and thermal parameters appear in Tables 1 and 2.*

Table 2. *Final fractional coordinates* ($\times 10^3$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^2$) *for the hydrogen atoms*

	x	y	z	U
H(11)	87 (5)	206 (10)	738 (3)	3·2 (17)
H(12)	175 (5)	367 (10)	730 (3)	3·0 (18)
H(21)	65 (6)	298 (11)	849 (3)	3·3 (21)
H(22)	207 (6)	276 (13)	839 (3)	7·5 (24)
H(3)	231 (6)	590 (11)	821 (3)	5·8 (22)
H(5)	90 (5)	690 (9)	740 (3)	3·8 (17)
H(61)	−157 (6)	739 (11)	751 (3)	5·1 (21)
H(62)	−70 (7)	911 (14)	762 (4)	6·9 (28)
H(71)	−135 (10)	887 (18)	666 (6)	14·8 (48)
H(72)	−7 (9)	854 (16)	671 (5)	11·6 (34)
H(111)	10 (6)	323 (11)	583 (3)	4·4 (22)
H(112)	−3 (5)	199 (11)	654 (3)	4·5 (21)
H(121)	−167 (9)	97 (18)	571 (5)	13·6 (37)
H(122)	−207 (7)	189 (11)	652 (4)	5·8 (24)
H(13)	−310 (6)	384 (10)	564 (3)	4·8 (21)
H(141)	−277 (10)	666 (21)	631 (6)	9·0 (50)
H(142)	−253 (7)	508 (14)	685 (4)	7·8 (28)
H(151)	−157 (6)	767 (12)	550 (3)	4·9 (23)
H(152)	−26 (7)	618 (13)	540 (3)	9·9 (27)
H(171)	−175 (9)	429 (17)	760 (5)	11·3 (41)
H(172)	−122 (8)	243 (17)	731 (5)	12·7 (35)
H(173)	−87 (6)	339 (12)	807 (4)	5·0 (23)
H(181)	151 (6)	868 (11)	891 (4)	7·5 (23)
H(182)	156 (6)	901 (12)	827 (4)	5·6 (25)
H(183)	39 (9)	952 (15)	853 (4)	8·7 (35)
H(191)	−61 (9)	493 (18)	877 (5)	11·9 (47)
H(192)	−23 (8)	675 (14)	910 (4)	5·0 (36)
H(193)	−120 (7)	704 (12)	868 (4)	7·7 (25)

Thermal motion analysis

The ellipsoids of thermal motion for the non-hydrogen atoms are shown in Fig. 1, a stereo view of the molecule produced by *ORTEP* (Johnson, 1965). The thermal motion has been analysed in terms of the rigid-body modes of translation (**T**), libration (**L**), and screw (**S**) motion by means of the computer program *MGTLS* (Schomaker & Trueblood, 1968).

Initially the entire molecule (excluding the hydrogen atoms) was analysed. The r.m.s. standard deviation in the temperature factors U_{ij} (Table 1) is 0·0050 Å^2, whereas the r.m.s. ΔU_{ij} is 0·0072 Å^2, indicating that the molecule as a whole is not a good rigid body. Examination of the individual ΔU_{ij} revealed significant independent motion of the acetoxy side chain. A second analysis excluding these four atoms gives an r.m.s. ΔU_{ij} value of 0·0051 Å^2, indicating that this portion of the molecule is a somewhat better approximation to a rigid body. The results of the two analyses are compiled in Table 3.* The rigid group shows nearly isotropic translational motion and anisotropic librational motion. Not unexpectedly the largest principal axis of **L**, L_1, is approximately parallel to the longest dimension of the molecule with an angle of 5·1° between L_1 and a line from C(4) to the midpoint of the C(8)–C(9) bond.

The appropriate bond distances and angles in the molecule (Tables 4 and 5) have been corrected for libration (Cruickshank, 1956, 1961) with shape parameters q^2 of 0·08 for all atoms; however, none of the values was altered significantly.

Table 4. *Bond lengths* (Å) *with estimated standard deviations in parentheses*

The C–H distances are in the range 0·79–1·34 Å with e.s.d.'s in the range 0·06–0·14 Å. The mean C–H distance is 1·06 Å.

C(1)–C(2)	1·519 (11)	C(8)—C(15)	1·578 (9)
C(1)–C(10)	1·536 (10)	C(9)—O(2)	1·437 (8)
C(2)–C(3)	1·490 (15)	C(9)—C(10)	1·588 (9)
C(3)–O(3)	1·471 (8)	C(9)—C(11)	1·538 (11)
C(3)–C(4)	1·535 (13)	C(10)–C(17)	1·551 (11)
C(4)–C(5)	1·580 (10)	C(11)–C(12)	1·550 (11)
C(4)–C(18)	1·529 (15)	C(12)–C(13)	1·532 (13)
C(4)–C(19)	1·556 (13)	C(13)–C(14)	1·536 (12)
C(5)–C(6)	1·507 (11)	C(13)–C(16)	1·527 (11)
C(5)–C(10)	1·591 (9)	C(15)–C(16)	1·514 (11)
C(6)–C(7)	1·530 (11)	C(16)–O(1)	1·203 (9)
C(7)–C(8)	1·554 (12)	C(20)–O(3)	1·318 (10)
C(8)–C(9)	1·540 (10)	C(20)–O(4)	1·178 (11)
C(8)–C(14)	1·553 (10)	C(20)–C(21)	1·524 (11)

Table 5. *Bond angles* (°) *with estimated standard deviations in parentheses*

(*a*) Non-hydrogen atoms

C(2)—C(1)–C(10)	114·2 (7)	C(8)—C(9)—O(2)	107·4 (6)
C(1)—C(2)–C(3)	109·5 (7)	C(10)–C(9)—C(11)	112·9 (5)
C(2)—C(3)–C(4)	114·6 (7)	C(10)–C(9)—O(2)	103·8 (5)
C(2)—C(3)–O(3)	109·7 (8)	C(11)–C(9)—O(2)	107·9 (5)
C(4)—C(3)–O(3)	108·0 (7)	C(9)—C(10)–C(1)	110·6 (5)
C(3)—C(4)–C(5)	106·8 (6)	C(9)—C(10)–C(5)	105·9 (4)
C(3)—C(4)–C(18)	109·5 (7)	C(9)—C(10)–C(17)	112·4 (5)
C(3)—C(4)–C(19)	111·4 (8)	C(1)—C(10)–C(5)	107·2 (5)
C(5)—C(4)–C(18)	107·0 (7)	C(1)—C(10)–C(17)	107·6 (5)
C(5)—C(4)–C(19)	113·6 (7)	C(5)—C(10)–C(17)	113·1 (6)
C(18)–C(4)–C(19)	108·4 (9)	C(9)—C(11)–C(12)	118·4 (7)
C(4)—C(5)–C(6)	114·6 (6)	C(11)–C(12)–C(13)	111·2 (7)
C(4)—C(5)–C(10)	116·1 (6)	C(12)–C(13)–C(14)	109·1 (6)
C(6)—C(5)–C(10)	110·1 (6)	C(12)–C(13)–C(16)	107·6 (6)
C(5)—C(6)–C(7)	110·9 (7)	C(14)–C(13)–C(16)	102·1 (7)
C(6)—C(7)–C(8)	110·6 (7)	C(13)–C(14)–C(8)	102·3 (6)
C(7)—C(8)–C(9)	111·9 (6)	C(8)—C(15)–C(16)	104·9 (6)
C(7)—C(8)–C(14)	112·5 (7)	C(13)–C(16)–O(1)	125·9 (7)
C(7)—C(8)–C(15)	108·4 (7)	C(15)–C(16)–O(1)	126·4 (7)
C(9)—C(8)–C(14)	114·1 (7)	C(13)–C(16)–C(15)	107·7 (6)
C(9)—C(8)–C(15)	111·3 (6)	O(3)—C(20)–C(21)	111·5 (7)
C(14)–C(8)–C(15)	97·7 (5)	O(4)—C(20)–C(21)	124·0 (8)
C(8)—C(9)–C(10)	114·5 (5)	O(3)—C(20)–O(4)	124·6 (8)
C(8)—C(9)–C(11)	109·9 (5)	C(3)—O(3)—C(20)	119·9 (6)

(*b*) Hydrogen atoms

Type	Range	Mean
R–C–H	93–125 (3–9)	112
H–C–H	90–125 (3–9)	106

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* A list of structure factors, Table 3 (thermal motion parameters) and Table 6 (intra- and intermolecular contacts) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30897 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

Fig. 1 shows a general view of the molecule displaying the crystallographic numbering scheme while Fig. 2 shows the packing arrangement viewed along **b**.

The molecule is characterized by a large amount of intramolecular steric crowding which largely determines the observed geometry. The pertinent C···C distances are listed in Table 6(*a*).* The detailed conformations of the various rings in the molecule are defined by the intra-annular torsion angles given in Table 7. Ring *A* is a normal chair slightly flattened at the junction to ring *B*. This flattening is most probably due to the transannular interaction between the methyl substituents on C(4) and C(10). Indeed the C(17)··· C(19) distance, 3·25 (1) Å, is much less than a normal van der Waals methyl···methyl separation of 4·0 Å. Similar ring *A* flattening has been observed in 4,4-dimethylandrostanes (Ferguson, Macaulay, Midgley, Robertson & Whalley, 1970; Rendle, 1972) and attrib-

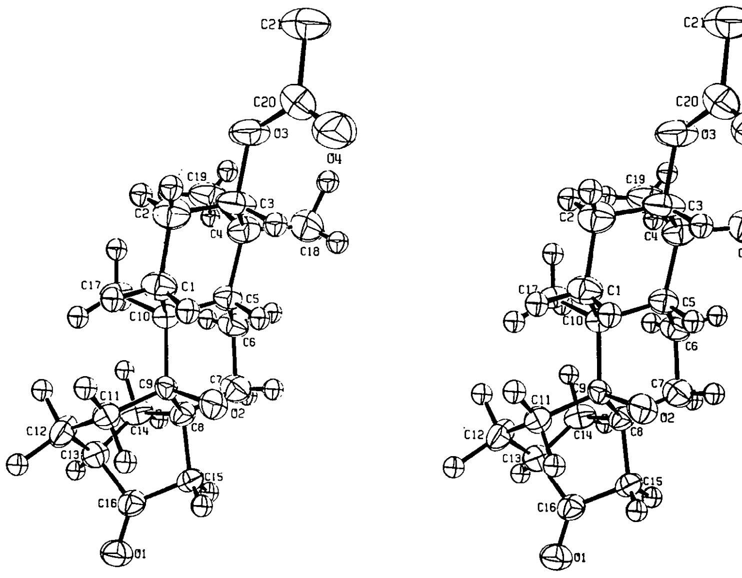

Fig. 1. Stereo diagram of 3-acetoxy-9-hydroxy-17-norkauran-16-one. The individual hydrogen labels are omitted for clarity. The thermal ellipsoids are at the 50 % probability level except for the hydrogen atoms which are assigned an arbitrary isotropic *B* of 2·0 Å^2.

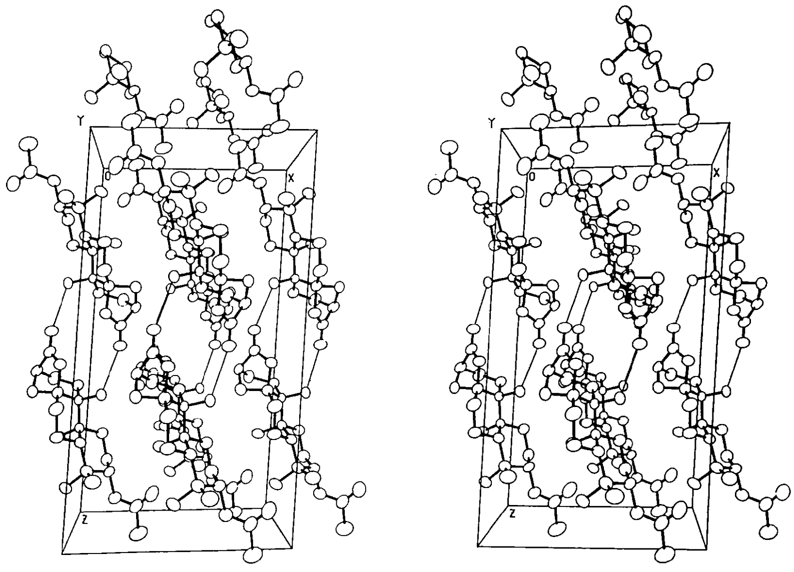

Fig. 2. Stereo diagram of the molecular packing of 3-acetoxy-9-hydroxy-17-norkauran-16-one.

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* See footnote on p. 1686.

Table 7. *Cis-torsion angles* (°)

(*a*) Ring *A*			
C(2)C(1)—C(10)C(5)	53·1 (7)	C(2)C(3)–C(4)C(5)	−55·4 (9)
C(10)C(1)–C(2)C(3)	−59·6 (9)	C(3)C(4)–C(5)C(10)	50·4 (8)
C(1)C(2)—C(3)C(4)	60·8 (9)	C(4)C(5)–C(10)C(1)	−49·9 (7)
(*b*) Ring *B*			
C(10)C(5)–C(6)C(7)	−65·3 (8)	C(7)C(8)–C(9)C(10)	50·7 (8)
C(5)C(6)—C(7)C(8)	59·2 (9)	C(8)C(9)–C(10)C(5)	−53·4 (6)
C(6)C(7)—C(8)C(9)	−50·9 (9)	C(6)C(5)–C(10)C(9)	59·8 (6)
(*c*) Ring *C*			
C(8)C(9)—C(11)C(12)	−34·4 (9)	C(12)C(13)–C(14)C(8)	70·4 (7)
C(9)C(11)—C(12)C(13)	39·7 (9)	C(9)C(8)—C(14)C(13)	−68·0 (7)
C(11)C(12)–C(13)C(14)	−58·4 (8)	C(14)C(8)—C(9)C(11)	49·8 (8)
(*d*) Ring *D*			
C(15)C(8)—C(14)C(13)	49·6 (7)	C(8)C(15)–C(16)C(13)	12·3 (8)
C(16)C(13)–C(14)C(8)	−43·3 (7)	C(14)C(8)–C(15)C(16)	−37·6 (7)
C(14)C(13)–C(16)C(15)	18·7 (8)		

uted to a rotation about the C(4)–C(5) bond to relieve the transannular interaction. A similar mechanism in the present structure is not unreasonable.

The conformation of ring *B* is also a chair which is flattened at the junction to ring *C*. As in ring *A* this flattening may be attributed to short transannular contacts between the C(17) methyl group and the *cis*-fused ring *C*. The pertinent distances are: C(17)···C(12) 3·41 (1), C(17)···C(13) 3·97 (1), C(17)···C(14) 3·25 (1) Å.

Although ring *C* also adopts a chair conformation it is distorted by the C(15)–C(16) bridge. The chair is considerably flattened at the C(11) end but increasingly puckered at the opposite C(14) end.

The five-membered ring *D* adopts a conformation closely approximating a half-chair slightly distorted towards a C(14) envelope. In more quantitative terms the conformation may be expressed in terms of the phase angle $\Delta = -8{\cdot}1°$ and the angle of puckering $\varphi_m = 50{\cdot}1°$ (Altona, Geise & Romers, 1968). The internal angles in the ring are all much less than tetrahedral, reflecting the strain inherent in five-membered rings. The remaining bond angles in the molecule are explicable in terms of the large amount of steric overcrowding and the relationship between them and the torsion angles precludes any detailed discussion.

The bond lengths for the most part do not differ significantly from the normal values for the particular bond type (Sutton, 1965). There are, however, some interesting exceptions. Two of the bonds involving C(10) are somewhat longer than a normal C(sp^3)–C(sp^3) bond. The increase in bond length of C(10)–C(5), 1·59 (1) and C(10)–C(9), 1·59 (1) Å may well reflect the tendency to relieve the high degree of steric interaction involving the C(17) methyl group. This would also explain the increase of the C(4)–C(5) bond length to 1·58 (1) Å. The weakening of the C(5)–C(10) and C(5)–C(4) bonds results in a strengthening of the C(5)–C(6) bond, and corresponding decrease in the bond length to 1·51 (1) Å. The C(2)–C(3) bond length, 1·49 (1) Å, is anomalously short, but there seems to be no apparent explanation. The average bond lengths are: C(sp^3)–C(sp^3) 1·545, C(sp^2–C(sp^3) 1·522, C(sp^3)–O(sp^3) 1·454, and C(sp^2)–O(sp^2) 1·191 Å.

In addition to the selected intramolecular contacts listed in Table 6(*a*),* the shorter intermolecular contacts between C and O atoms < 3·5 Å are given in Table 6(*b*).* Of note is a contact of 2·975 (7) Å between the hydroxyl oxygen O(2) and the carbonyl oxygen O(1) of a molecule related by the twofold axis (Fig. 2). The C(9)–O(2)···O(1) and O(2)···O(1)–C(16) angles (117·0 and 145·9° respectively) are within the limits expected for an O–H···O hydrogen bond (Hamilton & Ibers, 1968); however, the final difference synthesis showed only diffuse electron density between the two oxygen atoms so that any hydrogen bonding, if it does exist, is weak.

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* See footnote on p. 1686.

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The Crystal and Molecular Structure of $\Delta^{1,1'}$-Dicyclohexenyl Ketone

BY STEPHEN R. HOLBROOK AND DICK VAN DER HELM*

University of Oklahoma, Norman, Oklahoma 73069, *U.S.A.*

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Crystals of $\Delta^{1,1'}$-dicyclohexenyl ketone, $C_{13}H_{18}O$, are triclinic, space group $P\bar{1}$. The 2152 data were taken at −110°C. Cell dimensions are $a=9{\cdot}388$ (3), $b=8{\cdot}693$ (5), $c=9{\cdot}385$ (3) Å, $\alpha=104{\cdot}85$ (3), $\beta=113{\cdot}77$ (3), $\gamma=117{\cdot}16$ (2)°. The structure was determined by direct methods and has been refined to an R value of 5·1 %. The structure is partially disordered at room temperature. The crystals are colorless, but show a reversible photochromic change when subjected to near-ultraviolet radiation. Although the crystals undergo the same color change at low temperature, the reaction is not reversible and the crystals remain colored indefinitely at −110°C. Therefore, in addition to the data collected on the crystal in its colorless form, a data set was collected on the compound in its pink form at low temperature in an attempt to see a change in conformation or structure. A half-normal probability plot indicates no difference between the positional parameters derived from the two data sets. Both a short intramolecular and a short intermolecular distance are observed between the carbonyl oxygen atom and a hydrogen atom.

Introduction

Crystals of $\Delta^{1,1'}$-dicyclohexenyl ketone (DCK) undergo a reversible photochromic change when subjected to near-ultraviolet radiation. The crystals change from colorless to pink to a deep red depending on the length and intensity of irradiation. The process is readily reversible at room temperature, the crystals losing their color in a matter of minutes when removed from the exciting light. The formation of colored product with irradiation proceeds readily at low temperature, indicating a photochemical reaction. However, the loss of color is apparently a thermal process since the crystals when maintained at a low temperature (less than 0°C) after being irradiated, were seen to remain in the colored form indefinitely.

Several studies of photochromic reactions have been reported in the literature. Photochromism through partial torsion about an essential double bond in bianthrones was studied by Korenstein, Muskzat & Sharafy-Ozeri (1973). An irreversible photochromic reaction of *p*-nitrophenol was studied by X-ray crystallography by Coppens (1960). An intermolecular reaction was determined to be the basis of the photochromic change in this case. The crystal structures of of 2-(2′,4′-dinitrobenzyl)pyridine and 4-(2′,4′-dinitrobenzyl)pyridine have been determined (Seff & Trueblood, 1968; Otterson & Seff, 1974) to elucidate the reversible photochromic change observed in the former. An intramolecular tautomeric reaction in which a methylene hydrogen is transferred to the oxygen of the *o*-nitro group and then to the pyridine nitrogen is postulated on the basis of these structural determinations.

Lehr (1968) studied cyclization reactions of $\Delta^{1,1'}$ dicyclohexenyl ketone, a cross-conjugated dienone, in order to resolve the question of conrotatory *versus* disrotatory ring closure across C(2)–C(2′). Conrotatory closure was observed for the acid-catalyzed reaction, whereas disrotatory closure was observed for the photochemical reaction in solution. The reaction products for the photolysis in benzene indicated that hydrogen abstraction at C(6) [C(6′)], by the carbonyl O(8) may be involved in the cyclization reaction.

We have determined the structure of the colorless-form of $\Delta^{1,1'}$-dicyclohexenyl ketone at room temper-

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